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EPA Office of Compliance Sector Notebook Project
Profile of the Petroleum Refining Industry

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This report is one in a series of volumes published by the U.S. Environmental Protection Agency (EPA) to provide information of general interest regarding environmental issues associated with specific industrial sectors. The documents were developed under contract by Abt Associates (Cambridge, MA), and Booz-Allen & Hamilton, Inc. (McLean, VA). This publication may be **purchased** from the Superintendent of Documents, U.S. Government Printing Office. A listing of available Sector Notebooks and document numbers is included at the end of this document.

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List of Acronyms

AFS -	AIRS Facility Subsystem (CAA database)
AIRS -	Aerometric Information Retrieval System (CAA database)
BIFs -	Boilers and Industrial Furnaces (RCRA)
BOD -	Biochemical Oxygen Demand
CAA -	Clean Air Act
CAAA -	Clean Air Act Amendments of 1990
CERCLA -	Comprehensive Environmental Response, Compensation and Liability Act
CERCLIS -	CERCLA Information System
CFCs -	Chlorofluorocarbons
CO -	Carbon Monoxide
COD -	Chemical Oxygen Demand
CSI -	Common Sense Initiative
CWA -	Clean Water Act
D&B -	Dun and Bradstreet Marketing Index
ELP -	Environmental Leadership Program
EPA -	United States Environmental Protection Agency
EPCRA -	Emergency Planning and Community Right-to-Know Act
FIFRA -	Federal Insecticide, Fungicide, and Rodenticide Act
FINDS -	Facility Indexing System
HAPs -	Hazardous Air Pollutants (CAA)
HSDB -	Hazardous Substances Data Bank
IDEA -	Integrated Data for Enforcement Analysis
LDR -	Land Disposal Restrictions (RCRA)
LEPCs -	Local Emergency Planning Committees
MACT -	Maximum Achievable Control Technology (CAA)
MCLGs -	Maximum Contaminant Level Goals
MCLs -	Maximum Contaminant Levels
MEK -	Methyl Ethyl Ketone
MSDSs -	Material Safety Data Sheets
NAAQS -	National Ambient Air Quality Standards (CAA)
NAFTA -	North American Free Trade Agreement
NCDB -	National Compliance Database (for TSCA, FIFRA, EPCRA)
NCP -	National Oil and Hazardous Substances Pollution Contingency Plan
NEIC -	National Enforcement Investigation Center
NESHAP -	National Emission Standards for Hazardous Air Pollutants
NO ₂ -	Nitrogen Dioxide
NOV -	Notice of Violation
NO _x -	Nitrogen Oxides
NPDES -	National Pollution Discharge Elimination System (CWA)

NPL -	National Priorities List
NRC -	National Response Center
NSPS -	New Source Performance Standards (CAA)
OAR -	Office of Air and Radiation
OECA -	Office of Enforcement and Compliance Assurance
OPA -	Oil Pollution Act
OPPTS -	Office of Prevention, Pesticides, and Toxic Substances
OSHA -	Occupational Safety and Health Administration
OSW -	Office of Solid Waste
OSWER -	Office of Solid Waste and Emergency Response
OW -	Office of Water
P2 -	Pollution Prevention
PCS -	Permit Compliance System (CWA Database)
POTW -	Publicly Owned Treatments Works
RCRA -	Resource Conservation and Recovery Act
RCRIS -	RCRA Information System
SARA -	Superfund Amendments and Reauthorization Act
SDWA -	Safe Drinking Water Act
SEPs -	Supplementary Environmental Projects
SERCs -	State Emergency Response Commissions
SIC -	Standard Industrial Classification
SO ₂ -	Sulfur Dioxide
SO _x -	Sulfur Oxides
TOC -	Total Organic Carbon
TRI -	Toxic Release Inventory
TRIS -	Toxic Release Inventory System
TCRIS -	Toxic Chemical Release Inventory System
TSCA -	Toxic Substances Control Act
TSS -	Total Suspended Solids
UIC -	Underground Injection Control (SDWA)
UST -	Underground Storage Tanks (RCRA)
VOCs -	Volatile Organic Compounds

Message from the Administrator

I. INTRODUCTION TO THE SECTOR NOTEBOOK PROJECT

I.A. Summary of the Sector Notebook Project

Environmental policies based upon comprehensive analysis of air, water and land pollution are an inevitable and logical supplement to traditional single-media approaches to environmental protection. Environmental regulatory agencies are beginning to embrace comprehensive, multi-statute solutions to facility permitting, enforcement and compliance assurance, education/ outreach, research, and regulatory development issues. The central concepts driving the new policy direction are that pollutant releases to each environmental medium (air, water and land) affect every other, and that environmental strategies must actively identify and address these inter-relationships by designing policies for the "whole" facility. One way to achieve a whole facility focus is to design environmental policies for similar industrial facilities. By doing so, environmental concerns that are common to the manufacturing of similar products can be addressed in a comprehensive manner. Recognition of the need to develop the industrial "sector-based" approach within the EPA Office of Compliance led to the creation of this document.

The Sector Notebook Project was initiated by the Office of Compliance within the Office of Enforcement and Compliance Assurance (OECA) to provide its staff and managers with summary information for eighteen specific industrial sectors. As other EPA offices, states, the regulated community, environmental groups, and the public became interested in this project, the scope of the original project was expanded. The ability to design comprehensive, common sense environmental protection measures for specific industries is dependent on knowledge of several inter-related topics. For the purposes of this project, the key elements chosen for inclusion are: general industry information (economic and geographic); a description of industrial processes; pollution outputs; pollution prevention opportunities; Federal statutory and regulatory framework; compliance history; and a description of partnerships that have been formed between regulatory agencies, the regulated community and the public.

For any given industry, each topic listed above could alone be the subject of a lengthy volume. However, in order to produce a manageable document, this project focuses on providing summary information for each topic. This format provides the reader with a synopsis of each issue, and references where more in-depth information is available. Text within each profile was researched from a variety of sources, and was usually condensed from more detailed sources pertaining to specific topics. This

approach allows for a wide coverage of activities that can be further explored based upon the citations and references listed at the end of this profile. As a check on the information included, each notebook went through an external review process. The Office of Compliance appreciates the efforts of all those that participated in this process and enabled us to develop more complete, accurate and up-to-date summaries. Many of those who reviewed this notebook are listed as contacts in Section IX and may be sources of additional information. The individuals and groups on the list do not necessarily concur with all statements within this notebook.

I.B. Additional Information

Providing Comments

OECA's Office of Compliance plans to periodically review and update the notebooks and will make these updates available both in hard copy and electronically. If you have any comments on the existing notebook, or if you would like to provide additional information, please send a hard copy and computer disk to the EPA Office of Compliance, Sector Notebook Project, 401 M St., SW (2223-A), Washington, DC 20460. Comments can also be uploaded to the Enviro\$en\$e Bulletin Board or the Enviro\$en\$e World Wide Web for general access to all users of the system. Follow instructions in Appendix A for accessing these data systems. Once you have logged in, procedures for uploading text are available from the on-line Enviro\$en\$e Help System.

Adapting Notebooks to Particular Needs

The scope of the existing notebooks reflect an approximation of the relative national occurrence of facility types that occur within each sector. In many instances, industries within specific geographic regions or states may have unique characteristics that are not fully captured in these profiles. For this reason, the Office of Compliance encourages state and local environmental agencies and other groups to supplement or re-package the information included in this notebook to include more specific industrial and regulatory information that may be available. Additionally, interested states may want to supplement the "Summary of Applicable Federal Statutes and Regulations" section with state and local requirements. Compliance or technical assistance providers may also want to develop the "Pollution Prevention" section in more detail. Please contact the appropriate specialist listed on the opening page of this notebook if your office is interested in assisting us in the further development of the information or policies addressed within this volume.

If you are interested in assisting in the development of new notebooks for sectors not covered in the original eighteen, please contact the Office of Compliance at 202-564-2395.

II. INTRODUCTION TO THE PETROLEUM REFINING INDUSTRY

This section provides background information on the size, geographic distribution, employment, production, sales, and economic condition of the petroleum refining industry. The type of facilities described within the document are also described in terms of their Standard Industrial Classification (SIC) codes. Additionally, this section contains a list of the largest companies in terms of sales.

II.A. Introduction, Background, and Scope of the Notebook

Petroleum refining is one of the leading manufacturing industries in the United States in terms of its share of the total value of shipments of the U.S. economy. In relation to its economic importance, however, the industry is comprised of relatively few companies and facilities. The number of refineries operating in the U.S. can vary significantly depending on the information source. For example, in 1992, the Census Bureau counted 232 facilities and the Department of Energy reported 199 facilities. In addition, EPA's Toxic Release Inventory for 1993 identified 159 refineries. The differences lie in each organization's definition of a refinery. The Census Bureau's definition is based on the type of product that a facility produces and includes a number of very small operations producing a specific petroleum product, such as lubricating oils, from other refined petroleum products. These small facilities often employ fewer than 10 people and account for only one to two of the petroleum refining industry's total value of shipments.¹ In comparison to the typically much more complex, larger and more numerous crude oil processing refineries, these facilities with their smaller and relatively simple operations do not warrant the same level of attention from an economic and environmental compliance standpoint. Refineries recognized by the Department of Energy tend to be only the larger facilities which process crude oil into refined petroleum products.^a

Whenever possible, the facility level data used in this notebook are based on those refineries identified by the Department of Energy's Energy Information Administration. Since the Energy and Information

^a Variations in facility counts occur across data sources due to many factors including, reporting and definitional differences. This notebook does not attempt to reconcile these differences, but rather reports the data as they are maintained by each source.

Administration does not collect economic, employment and environmental release information on refineries, other facility level data sources were used. Thus, employment and sales data are based on information collected through the Bureau of Census' Census of Manufacturers for 1992 and environmental release information was obtained from EPA's Toxic Release Inventory.

II.B. Characterization of the Petroleum Refining Industry

II.B.1. Product Characterization

Petroleum refining is the physical, thermal and chemical separation of crude oil into its major distillation fractions which are then further processed through a series of separation and conversion steps into finished petroleum products. The primary products of the industry fall into three major categories: fuels (motor gasoline, diesel and distillate fuel oil, liquefied petroleum gas, jet fuel, residual fuel oil, kerosene, and coke); finished nonfuel products (solvents, lubricating oils, greases, petroleum wax, petroleum jelly, asphalt, and coke); and chemical industry feedstocks (naphtha, ethane, propane, butane, ethylene, propylene, butylenes, butadiene, benzene, toluene, and xylene). These petroleum products comprise about 40 percent of the total energy consumed in the U.S.² (based on BTUs consumed) and are used as primary input to a vast number of products, including: fertilizers, pesticides, paints, waxes, thinners, solvents, cleaning fluids, detergents, refrigerants, anti-freeze, resins, sealants, insulations, latex, rubber compounds, hard plastics, plastic sheeting, plastic foam and synthetic fibers.³ About 90 percent of the petroleum products used in the U.S. are fuels with motor gasoline accounting for about 43 percent of the total⁴ (Exhibit 1).

The Standard Industrial Classification (SIC) code established by the Bureau of Census to track the flow of goods and services within the economy is 29 for the Petroleum Refining and Related Industries. The petroleum refining industry is classified as SIC 2911, which includes the production of petroleum products through distillation and fractionation of crude oil, redistillation of unfinished petroleum derivatives, cracking, or other processes. The related industries under SIC 29 are: 2951, Asphalt Paving Mixtures and Blocks; 2952, Asphalt Felts and Coatings; 2992, Lubricating Oils and Greases; and 2999, Petroleum and Coal Products, Not Elsewhere Classified. Certain products that are produced by the petroleum refining industry are also produced by other industries, including: 2865, Cyclic Organic Crudes and Intermediates, and Organic Dyes and Pigments; 2869, Industrial Organic Chemicals; 2819, Industrial Inorganic Chemicals, Not Elsewhere Classified; 2821, Plastic Materials, Synthetic

Resins, Nonvulcanizable Elastomers; 2873, Nitrogenous Fertilizers; 4613, Refined Petroleum Pipelines; and 5171, Petroleum Bulk Stations and Terminals.⁵

II.B.2. Industry Size and Geographic Distribution

Generally, the petroleum refining industry can be characterized by a relatively small number of large facilities. The Department of Energy reported 176 operating petroleum refineries in 1994 with a total crude oil distillation capacity of approximately 15 million barrels per day. Most U.S. crude oil distillation capacity is owned by large, integrated companies with multiple high capacity refining facilities. Small refineries with capacities below 50,000 barrels per day, however, do play a significant role in the industry, making up about half of all facilities, but only 14 percent of the total crude distillation capacity.⁶

A relatively small number of people are employed by the petroleum refining industry in relation to its economic importance. The Bureau of the Census estimates that 75,000 people were directly employed by the industry in 1992.⁷ However, the industry also indirectly employs a significant number of outside contractors for many refinery operations, both routine and non-routine. The value of product shipments sold by refining establishments was estimated to be \$136 billion in 1992. This accounts for about 4 percent of the value of shipments for the entire U.S. manufacturing sector.⁸ Based on the number of people directly employed by refineries, the industry has a high value of shipments per employee of \$1.8 million. In comparison, the value of shipments per employee for the steel manufacturing industry was \$245,000 for the same year.⁹

The Bureau of Census employment data for 1992 (the most recent facility-based employment data available) indicated that 60 percent of petroleum refineries had over 100 employees¹⁰ (Exhibit 2).

Exhibit 2: Large Facilities Dominate Petroleum Refining Industry		
Employees per Facility	Number of Facilities	Percentage of Facilities
1-4	17	7%
5-9	7	3%
10-19	11	5%
20-49	35	15%
50-99	22	10%
100-249	45	19%
250-499	49	21%
500-999	26	11%
1000-2499	20	9%
Total	232	100%
Source: Census of Manufacturers, 1992.		

For reasons of efficiency in transporting crude oil feed stocks and finished products, petroleum refineries typically were sited near crude oil sources (onshore petroleum terminals, oil and gas extraction areas) or consumers (heavily industrialized areas). Consequently, the distribution of facilities is more concentrated along the Gulf Coast and near the heavily industrialized areas of both east and west coasts (Exhibits 3 and 4). Based on Department of Energy data for 1994, 78 percent of the U.S. crude oil distillation capacity (which is indicative of the amount of crude oil processed) is located in just ten states¹¹ (Exhibit 3).

Exhibit 3: Crude Oil Distillation Capacity Located Primarily Along Coasts			
State	Number of Operable Refineries	Crude Distillation Capacity (thousand barrels per day)	Percent of U.S. Total Distillation Capacity
Texas	30	3,764	25%
Louisiana	19	2,360	16%
California	25	1,882	12%
Illinois	7	956	6%
Pennsylvania	8	655	4%
Washington	6	524	3%
Ohio	4	430	3%
New Jersey	4	462	3%
Indiana	2	421	3%
Oklahoma	7	404	3%
Subtotal	112	11,858	78%
Other States (also includes Virgin Islands and Puerto Rico)	64	3,355	22%
U.S. Total	176	15,213	100%
Source: U.S. Department of Energy/Energy Information Administration, 1994.			

(Source: U.S. EPA Toxic Release Inventory Database, 1993.)

Ward's Business Directory of U.S. Private and Public Companies, produced by Gale Research Inc., compiles financial data on U.S. companies including those operating within the petroleum refining industry. Ward's ranks U.S. companies, whether they are a parent company, subsidiary or division, by sales volume within the 4-digit SIC codes that they have been assigned as their primary activity. Readers should note that: 1) companies are assigned a 4-digit SIC that most closely resembles their principal industry; and 2) sales figures include total company sales, including sales derived from subsidiaries and operations not related to petroleum refining. Additional sources of company specific financial information include Standard & Poor's *Stock Report Services*, Dun & Bradstreet's *Million Dollar Directory*, Moody's Manuals, and annual reports.

Exhibit 5: Top U.S. Companies with Petroleum Refining Operations		
Rank^a	Company^b	1993 Sales (millions of dollars)
1	Exxon Corporation - Irving TX	102,847
2	Mobil Corporation - Fairfax, VA	56,910
3	El du Pont de Nemours and Co. (Conoco Inc., Subsidiary) - Wilmington, DE	38,031
4	Texaco Inc. - White Plains, NY	37,271
5	Chevron Corporation - San Francisco, CA	35,523
6	Amoco Oil Corporation - Chicago, IL	22,320
7	Shell Oil Company - Houston, TX	22,201
8	Atlantic Richfield Company - Los Angeles, CA	18,922
9	BP America Incorporated - Cleveland, OH	16,200
10	Caltex Petroleum Corporation - Dallas, TX	15,100
<p>Note: ^a When Ward's Business Directory listed both a parent and subsidiary in the top ten, only the parent company is presented above to avoid double counting sales volumes. Not all sales can be attributed to the companies' petroleum refining operations. ^b Companies shown listed SIC 2911 as primary activity.</p>		
Source: Ward's Business Directory of U.S. Private and Public Companies - 1993.		

II.B.3. Economic Trends

The United States is a net importer of crude oil and petroleum products. In 1994, imports accounted for more than 50 percent of the crude oil used in the U.S. and about 10 percent of finished petroleum products.¹² The imported share of crude oil is expected to increase as U.S. demand for petroleum products increases and the domestic production of crude oil declines. Imported finished petroleum products serve specific market niches arising from logistical considerations, regional shortages, and long-term trade relations between suppliers and refiners. Exports of refined petroleum products, which primarily consist of petroleum coke, residual fuel oil, and distillate fuel oil, account for about four percent of the U.S. refinery output. Exports of crude oil produced in the U.S. account for about one percent of the total U.S. crude oil produced and imported.¹³

The petroleum refining industry in the U.S. has felt considerable economic pressures in the past decade arising from a number of factors including: increased costs of labor; compliance with new safety and environmental regulations; and the elimination of government subsidies through the Crude Oil Entitlements Program which had encouraged smaller refineries to add capacity throughout the 1970s.¹⁴ A rationalization period began after crude oil pricing and entitlements were decontrolled in early 1981. The market determined that there was surplus capacity and the margins dropped to encourage the closure of the least efficient capacity. Reflecting these pressures, numerous facilities have closed in recent years.¹⁵ Between 1982 and 1994, the number of U.S. refineries as determined by the Department of Energy dropped from 301 to 176. Most of these closures have involved small facilities refining less than 50,000 barrels of crude oil per day. Some larger facilities, however, have also closed in response to economic pressures.¹⁶ Industry representatives cited complying with the increasing environmental regulations, particularly, the requirements of the Clean Air Act Amendments of 1990, as the most important factor affecting petroleum refining in the 1990s.¹⁷ Despite the closing of refineries in recent years, total refinery output of finished products has remained relatively steady with slight increases in the past two years. Increases in refinery outputs are attributable to higher utilization rates of refinery capacity, and to incremental additions to the refining capacity at existing facilities as opposed to construction of new refineries.¹⁸

Demand for refined petroleum products is expected to increase slowly through 1998 with the growth of the U.S. economy. The rate of increase will average about 1.5 percent per year, which is slower than the expected

growth of the economy. This slower rate of increase of demand will be due to increasing prices of petroleum products as a result of conservation, the development of substitutes for petroleum products, and rising costs of compliance with environmental and safety requirements.¹⁹

Recent and future environmental and safety regulatory changes are expected to force the petroleum refining industry to make substantial investments in upgrading certain refinery processes to reduce emissions and alter product compositions. For example, industry estimates of the capital costs to comply with the 1990 Clean Air Act Amendments, which mandates specific product compositions are about \$35 to \$40 billion.²⁰ There is concern that in some cases it may be more economical for some refineries to close down partially or entirely rather than upgrade facilities to meet the new standards. In fact, the U.S. Departments of Energy and Commerce expect refinery shutdowns to continue through the 1990s; however, total crude oil distillation capacity is expected to remain relatively stable as a result of increased capacity and utilization rates at existing facilities. Increases in demand for finished petroleum products will be filled by increased imports.

III. INDUSTRIAL PROCESS DESCRIPTION

This section describes the major industrial processes within the petroleum refining industry, including the materials and equipment used, and the processes employed. The section is designed for those interested in gaining a general understanding of the industry, and for those interested in the inter-relationship between the industrial process and the topics described in subsequent sections of this profile -- pollutant outputs, pollution prevention opportunities, and Federal regulations. This section does not attempt to replicate published engineering information that is available for this industry. Refer to Section IX for a list of reference documents that are available.

This section specifically contains a description of commonly used production processes, associated raw materials, the byproducts produced or released, and the materials either recycled or transferred off-site. This discussion, coupled with schematic drawings of the identified processes, provide a concise description of where wastes may be produced in the process. This section also describes the potential fate (via air, water, and soil pathways) of these waste products.

III.A. Industrial Processes in the Petroleum Refining Industry

Crude oil is a mixture of many different hydrocarbons and small amounts of impurities. The composition of crude oil can vary significantly depending on its source. Petroleum refineries are a complex system of multiple operations and the operations used at a given refinery depend upon the properties of the crude oil to be refined and the desired products. For these reasons, no two refineries are alike. Portions of the outputs from some processes are re-fed back into the same process, fed to new processes, fed back to a previous process, or blended with other outputs to form finished products (Exhibit 6). The major unit operations typically involved at petroleum refineries are described briefly below. In addition to those listed below, there are also many special purpose processes that cannot be described here and which may play an important role in a facility's efforts to comply with pollutant discharge and product specification requirements.

Refining crude oil into useful petroleum products can be separated into two phases and a number of supporting operations. The first phase is desalting of crude oil and the subsequent distillation into its various components or "fractions" (Section III.A.1). The second phase is made up of three different types of "downstream" processes: combining, breaking, and reshaping (Section III.A.2). Downstream processes convert some of the distillation fractions into petroleum products (residual fuel oil, gasoline, kerosene, etc.) through any combination of different cracking, coking, reforming, and alkylation processes. Supporting operations may include wastewater treatment, sulfur recovery, additive production, heat exchanger cleaning, blowdown systems, blending of products, and storage of products (Section III.A.3). Refinery pollutant outputs are discussed in more detail in Section III.B.

III.A.1. Crude Oil Distillation and Desalting

One of the most important operations in a refinery is the initial distillation of the crude oil into its various boiling point fractions. Distillation involves the heating, vaporization, fractionation, condensation, and cooling of feedstocks. This section discusses the atmospheric and vacuum distillation processes which when used in sequence result in lower costs and higher efficiencies. This section also discusses the important first step of desalting the crude oil prior to distillation.

Desalting

Before separation into fractions, crude oil usually must first be treated to remove corrosive salts. The desalting process also removes some of the metals and suspended solids which cause catalyst deactivation. Desalting involves the mixing of heated crude oil with water (about three to 10 percent of the crude oil volume) so that the salts are dissolved in the water.²¹ The water must then be separated from the crude oil in a separating vessel by adding demulsifier chemicals to assist in breaking the emulsion and/or, more commonly, by applying a high potential electric field across the settling vessel to coalesce the polar salt water droplets. The desalting process creates an oily desalter sludge and a high temperature salt water waste stream which is typically added to other process wastewaters for treatment in the refinery wastewater treatment facilities. The water used in crude desalting is often untreated or partially treated water from other refining process water sources.²²

Atmospheric Distillation

The desalted crude oil is then heated in a heat exchanger and furnace to about 750 degrees (F) and fed to a vertical, distillation column at atmospheric pressure where most of the feed is vaporized and separated into its various fractions by condensing on 30 to 50 fractionation trays, each corresponding to a different condensation temperature. The lighter fractions condense and are collected towards the top of the column. Heavier fractions, which may not vaporize in the column, are further separated later by vacuum distillation. Within each atmospheric distillation tower, a number of side streams (at least four) of low-boiling point components are removed from the tower from different trays. These low-boiling point mixtures are in equilibrium with heavier components which must be removed. The side streams are each sent to a different small stripping tower containing four to 10 trays with steam injected under the bottom tray. The steam strips the light-end components from the heavier components and both the steam and light-ends are fed back to the atmospheric distillation tower above the corresponding side stream draw tray.²³ Fractions obtained from atmospheric distillation include naphtha, gasoline, kerosene, light fuel oil, diesel oils, gas oil, lube distillate, and heavy bottoms. Most of these can be sold as finished products, or blended with products from downstream processes. Another product produced in atmospheric distillation, as well as many other refinery processes, is the light, noncondensable refinery fuel gas (mainly methane and ethane). Typically this gas also contains hydrogen sulfide and ammonia gases. The mixture of these gases is known as "sour gas" or "acid gas." The sour gas is sent to the refinery sour gas treatment system which separates the fuel gas so that it can be used as fuel in the refinery heating furnaces. Air emissions during atmospheric distillation arise from the combustion of fuels in the furnaces to heat the crude oil, process vents and fugitive emissions. Oily sour water (condensed steam containing hydrogen sulfate and ammonia) and oil is also generated in the fractionators²⁴ (Exhibit 7).

Vacuum Distillation

Heavier fractions from the atmospheric distillation unit that cannot be distilled without cracking under its pressure and temperature conditions are vacuum distilled. Vacuum distillation is simply the distillation of petroleum fractions at a very low pressure (0.2 to 0.7 psia) to increase volatilization and separation. In most systems, the vacuum inside the fractionator is maintained with steam ejectors and vacuum pumps,

barometric condensers or surface condensers. The injection of superheated steam at the base of the vacuum fractionator column further reduces the partial pressure of the hydrocarbons in the tower, facilitating vaporization and separation. The heavier fractions from the vacuum distillation column are processed downstream into more valuable products through either cracking or coking operations (See Section III.A.2.).²⁵

A potential source of emissions from distillation of crude oil are the combustion of fuels in the furnace and some light gases leaving the top of the condensers on the vacuum distillation column. A certain amount of noncondensable light hydrocarbons and hydrogen sulfide pass through the condenser to a hot well, and then are discharged to the refinery sour fuel system or are vented to a process heater, flare or another control device to destroy hydrogen sulfide. The quantity of these emissions depends on the size of the unit, the type of feedstock, and the cooling water temperature.²⁶ If barometric condensers are used in vacuum distillation, significant amounts of oily wastewater can be generated. Vacuum pumps and surface condensers have largely replaced barometric condensers in many refineries to eliminate this oily wastewater stream. Oily sour water is also generated in the fractionators.²⁷

III.A.2. Downstream Processing

Certain fractions from the distillation of crude oil are further refined in thermal cracking (visbreaking), coking, catalytic cracking, catalytic hydrocracking, hydrotreating, alkylation, isomerization, polymerization, catalytic reforming, solvent extraction, merox, dewaxing, propane deasphalting and other operations. These downstream processes change the molecular structure of hydrocarbon molecules either by breaking them into smaller molecules, joining them to form larger molecules, or reshaping them into higher quality molecules. For many of the operations discussed below, a number of different techniques are used in the industry. While the major techniques used for each process are described, it was not possible to discuss all of the different processes currently in use.

Thermal Cracking/Visbreaking

Thermal cracking, or visbreaking, uses heat and pressure to break large hydrocarbon molecules into smaller, lighter molecules. The process has been largely replaced by catalytic cracking and some refineries no longer employ thermal cracking. Both processes reduce the production of less valuable products such as heavy fuel oil and cutter stock and increase the feed stock to the catalytic cracker and gasoline yields. In thermal cracking, heavy gas oils and residue from the vacuum distillation process are

typically the feed stocks. The feed stock is heated in a furnace or other thermal unit to up to 1,000 degrees (F) and then fed to a reaction chamber which is kept at a pressure of about 140 psig. Following the reactor step, the process stream is mixed with a cooler recycle stream, which stops the cracking reactions. The product is then fed to a flasher chamber, where pressure is reduced and lighter products vaporize and are drawn off. The lighter products are fed to a fractionating tower where the various fractions are separated. The "bottoms" consist of heavy residue, part of which is recycled to cool the process stream leaving the reaction chamber; the remaining bottoms are usually blended into residual fuel (Exhibit 8).²⁸

Air emissions from thermal cracking include emissions from the combustion of fuels in the process heater, vents, and fugitive emissions.²⁹ A sour water stream is generated in the fractionator.³⁰

Coking

Coking is a cracking process used primarily to reduce refinery production of low-value residual fuel oils to transportation fuels, such as gasoline and diesel. As part of the upgrading process, coking also produces petroleum coke, which is essentially solid carbon with varying amounts of impurities, and is used as a fuel for power plants if the sulfur content is low enough. Coke also has nonfuel applications as a raw material for many carbon and graphite products including anodes for the production of aluminum, and furnace electrodes for the production of elemental phosphorus, titanium dioxide, calcium carbide and silicon carbide.³¹ A number of different processes are used to produce coke; "delayed coking" is the most widely used today, but "fluid coking" is expected to be an important process in the future. Fluid coking produces a higher grade of coke which is increasingly in demand. In delayed coking operations, the same basic process as thermal cracking is used except feed streams are allowed to react longer without being cooled. The delayed coking feed stream of residual oils from various upstream processes is first introduced to a fractionating tower where residual lighter materials are drawn off and the heavy ends are condensed. The heavy ends are removed and heated in a furnace to about 900 - 1,000 degrees (F) and then fed to an insulated vessel called a coke drum where the coke is formed. When the coke drum is filled with product, the feed is switched to an empty parallel drum. Hot vapors from the coke drums, containing cracked lighter hydrocarbon products, hydrogen sulfide, and ammonia, are fed back to the fractionator where they can be treated in the sour gas treatment system or drawn off as intermediate products. Steam is then injected into the full coke drum to remove hydrocarbon vapors, water is injected to cool the coke, and the coke is removed. Typically, high pressure water jets are used to cut the coke from the drum (Exhibit 9).³²

Air emissions from coking operations include the process heater flue gas emissions, fugitive emissions and emissions that may arise from the removal of the coke from the coke drum. The injected steam is condensed and the remaining vapors are typically flared. Wastewater is generated from the coke removal and cooling operations and from the steam injection. In addition, the removal of coke from the drum can release particulate emissions and any remaining hydrocarbons to the atmosphere.

Catalytic Cracking

Catalytic cracking uses heat, pressure and a catalyst to break larger hydrocarbon molecules into smaller, lighter molecules. Catalytic cracking has largely replaced thermal cracking because it is able to produce more gasoline with a higher octane and less heavy fuel oils and light gases. Feed stocks are light and heavy oils from the crude oil distillation unit which are processed primarily into gasoline as well as some fuel oil and light gases. Most catalysts used in catalytic cracking consist of mixtures of crystalline synthetic silica-alumina, termed "zeolites," and amorphous synthetic silica-alumina. The catalytic cracking processes, as well as most other refinery catalytic processes, produce coke which collects on the catalyst surface and diminishes its catalytic properties. The catalyst, therefore, needs to be regenerated continuously or periodically essentially by burning the coke off the catalyst at high temperatures. The method and frequency in which catalysts are regenerated are a major factor in the design of catalytic cracking units. A number of different catalytic cracking designs are currently in use in the U.S., including fixed-bed reactors, moving-bed reactors, fluidized-bed reactors, and once-through units. The fluidized- and moving-bed reactors are by far the most prevalent.³³

Fluidized-bed catalytic cracking units (FCCUs) are by far the most common catalytic cracking units. In the fluidized-bed process, oil and oil vapor pre-heated to 500 to 800 degrees (F) is contacted with hot catalyst at about 1,300 (F) either in the reactor itself or in the feed line (riser) to the reactor. The catalyst is in a fine, granular form which, when mixed with the vapor, has many of the properties of a fluid. The fluidized catalyst and the reacted hydrocarbon vapor separate mechanically in the reactor and any oil remaining on the catalyst is removed by steam stripping. The cracked oil vapors are then fed to a fractionation tower where the various desired fractions are separated and collected. The catalyst flows into a separate vessel(s) for either single- or two-stage regeneration by burning off the coke deposits with air (Exhibit 10).³⁴

In the moving-bed process, oil is heated to up to 1,300 degrees (F) and is passed under pressure through the reactor where it comes into contact with

a catalyst flow in the form of beads or pellets. The cracked products then flow to a fractionating tower where the various compounds are separated and collected. The catalyst is regenerated in a continuous process where deposits of coke on the catalyst are burned off. Some units also use steam to strip remaining hydrocarbons and oxygen from the catalyst before being fed back to the oil stream. In recent years moving-bed reactors have largely been replaced by fluidized-bed reactors.³⁵

Catalytic cracking is one of the most significant sources of air pollutants at refineries. Air emissions from catalytic cracking operations include: the process heater flue gas emissions, fugitive emissions, and emissions generated during regeneration of the catalyst. Relatively high concentrations of carbon monoxide can be produced during regeneration of the catalyst which is typically converted to carbon dioxide either in the regenerator or further downstream in a carbon monoxide waste heat boiler.³⁶ In addition, a significant amount of fine catalyst dust is produced in FCCUs as a result of the constant movement of the catalyst grains against each other. Much of this dust, consisting primarily of alumina and relatively small amounts of nickel, is carried with the carbon monoxide stream to the carbon monoxide burner. The catalyst dust is then separated from the resulting carbon dioxide stream via cyclones and/or electrostatic precipitators and is sent off-site for disposal or treatment.³⁷ Generated wastewater is typically sour water from the fractionator containing some oil and phenols. Wastewater containing metal impurities from the feed oil can also be generated from the steam used to purge and regenerate catalysts.³⁸

Catalytic Hydrocracking

Catalytic hydrocracking normally utilizes a fixed-bed catalytic cracking reactor with cracking occurring under substantial pressure (1,200 to 2,000 psig) in the presence of hydrogen. Feedstocks to hydrocracking units are often those fractions that are the most difficult to crack and cannot be cracked effectively in catalytic cracking units. These include: middle distillates, cycle oils, residual fuel oils and reduced crudes. The hydrogen suppresses the formation of heavy residual material and increases the yield of gasoline by reacting with the cracked products. However, this process also breaks the heavy, sulfur and nitrogen bearing hydrocarbons and releases these impurities to where they could potentially foul the catalyst. For this reason, the feedstock is often first hydrotreated to remove impurities before being sent to the catalytic hydrocracker. Sometimes hydrotreating is accomplished by using the first reactor of the hydrocracking process to remove impurities. Water also has a detrimental

effect on some hydrocracking catalysts and must be removed before being fed to the reactor. The water is removed by passing the feed stream through a silica gel or molecular sieve dryer. Depending on the products desired and the size of the unit, catalytic hydrocracking is conducted in either single stage or multi-stage reactor processes. Most catalysts consist of a crystalline mixture of silica-alumina with small amounts of rare earth metals (Exhibit 11).³⁹

Hydrocracking feedstocks are usually first hydrotreated to remove the hydrogen sulfide and ammonia that will poison the catalyst. Sour gas and sour water streams are produced at the fractionator, however, if the hydrocracking feedstocks are first hydrotreated to remove impurities, both streams will contain relatively low levels of hydrogen sulfide and ammonia. Hydrocracking catalysts are typically regenerated off-site after two to four years of operation. Therefore, little or no emissions are generated from the regeneration processes. Air emissions arise from the process heater, vents, and fugitive emissions.^{40,41}

Hydrotreating/Hydroprocessing

Hydrotreating and hydroprocessing are similar processes used to remove impurities such as sulfur, nitrogen, oxygen, halides and trace metal impurities that may deactivate process catalysts. Hydrotreating also upgrades the quality of fractions by converting olefins and diolefins to paraffins for the purpose of reducing gum formation in fuels. Hydroprocessing, which typically uses residuals from the crude distillation units, also cracks these heavier molecules to lighter more saleable products. Both hydrotreating and hydroprocessing units are usually placed upstream of those processes in which sulfur and nitrogen could have adverse effects on the catalyst, such as catalytic reforming and hydrocracking units. The processes utilize catalysts in the presence of substantial amounts of hydrogen under high pressure and temperature to react the feedstocks and impurities with hydrogen. The reactors are nearly all fixed-bed with catalyst replacement or regeneration done after months or years of operation often at an off-site facility.⁴² In addition to the treated products, the process produces a stream of light fuel gases, hydrogen sulfide, and ammonia. The treated product and hydrogen-rich gas are cooled after they leave the reactor before being separated. The hydrogen is recycled to the reactor.

The off-gas stream may be very rich in hydrogen sulfide and light fuel gas. The fuel gas and hydrogen sulfide are typically sent to the sour gas

treatment unit and sulfur recovery unit. Catalysts are typically cobalt or molybdenum oxides on alumina, but can also contain nickel and tungsten. Air emissions from hydrotreating may arise from process heater flue gas, vents, and fugitive emissions (Exhibit 12).⁴³

Alkylation

Alkylation is used to produce a high octane gasoline blending stock from the isobutane formed primarily during catalytic cracking and coking operations, but also from catalytic reforming, crude distillation and natural gas processing. Alkylation joins an olefin and an isoparaffin compound using either a sulfuric acid or hydrofluoric acid catalyst. The products are alkylates including propane and butane liquids. When the concentration of acid becomes less than 88 percent, some of the acid must be removed and replaced with stronger acid. In the hydrofluoric acid process, the slip stream of acid is redistilled. Dissolved polymerization products are removed from the acid as a thick dark oil. The concentrated hydrofluoric acid is recycled and the net consumption is about 0.3 pounds per barrel of alkylates produced. Hydrofluoric acid alkylation units require special engineering design, operator training and safety equipment precautions to protect operators from accidental contact with hydrofluoric acid which is an extremely hazardous substance. In the sulfuric acid process, the sulfuric acid removed must be regenerated in a sulfuric acid plant which is generally not a part of the alkylation unit and may be located off-site. Spent sulfuric acid generation is substantial; typically in the range of 13 to 30 pounds per barrel of alkylate.⁴⁴ Air emissions from the alkylation process may arise from process vents and fugitive emissions.

Isomerization

Isomerization is used to alter the arrangement of a molecule without adding or removing anything from the original molecule. Typically, paraffins (butane or pentane from the crude distillation unit) are converted to isoparaffins having a much higher octane. Isomerization reactions take place at temperatures in the range of 200 to 400 degrees (F) in the presence of a catalyst that usually consists of platinum on a base material. Two types of catalysts are currently in use. One requires the continuous addition of small amounts of organic chlorides which are converted to hydrogen chloride in the reactor. In such a reactor, the feed must be free of oxygen sources including water to avoid deactivation and corrosion problems. The other type of catalyst uses a molecular sieve base and does not require a dry and oxygen free feed. Both types of isomerization catalysts require an atmosphere of hydrogen to minimize coke deposits; however, the consumption of hydrogen is negligible. Catalysts typically need to be replaced about every two to three years or longer.⁴⁵ Platinum

is then recovered from the used catalyst off-site. Light ends are stripped from the product stream leaving the reactor and are then sent to the sour gas treatment unit. Some isomerization units utilize caustic treating of the light fuel gas stream to neutralize any entrained hydrochloric acid. This will result in a calcium chloride (or other salts) waste stream. Air emissions may arise from the process heater, vents and fugitive emissions.⁴⁶ Wastewater streams include caustic wash and sour water.⁴⁷

Polymerization

Polymerization is occasionally used to convert propene and butene to high octane gasoline blending components. The process is similar to alkylation in its feed and products, but is often used as a less expensive alternative to alkylation. The reactions typically take place under high pressure in the presence of a phosphoric acid catalyst. The feed must be free of sulfur, which poisons the catalyst; basic materials, which neutralize the catalyst; and oxygen, which affects the reactions. The propene and butene feed is washed first with caustic to remove mercaptans (molecules containing sulfur), then with an amine solution to remove hydrogen sulfide, then with water to remove caustics and amines, and finally dried by passing through a silica gel or molecular sieve dryer.⁴⁸ Air emissions of sulfur dioxide may arise during the caustic washing operation. Spent catalyst, which typically is not regenerated, is occasionally disposed as a solid waste.⁴⁹ Wastewater streams will contain caustic wash and sour water with amines and mercaptans.⁵⁰

Catalytic Reforming

Catalytic reforming uses catalytic reactions to process primarily low octane heavy straight run (from the crude distillation unit) gasolines and naphthas into high octane aromatics (including benzene). There are four major types of reactions which occur during reforming processes: 1) dehydrogenation of naphthenes to aromatics; 2) dehydrocyclization of paraffins to aromatics; 3) isomerization; and 4) hydrocracking. The dehydrogenation reactions are very endothermic, requiring that the hydrocarbon stream be heated between each catalyst bed. All but the hydrocracking reaction release hydrogen which can be used in the hydrotreating or hydrocracking processes. Fixed-bed or moving bed processes are utilized in a series of three to six reactors. Feedstocks to catalytic reforming processes are usually hydrotreated first to remove sulfur, nitrogen and metallic contaminants. In continuous reforming processes, catalysts can be regenerated one reactor at a time, once or twice per day, without disrupting the operation of the unit. In semi regenerative units, regeneration of all reactors can be carried out simultaneously after

three to 24 months of operation by first shutting down the process.⁵¹ Because the recent reformulated gasoline rules have limited the allowable amount of benzene in gasoline (Section VI.B), catalytic reforming is being used less as an octane enhancer than in past years.

Air emissions from catalytic reforming arise from the process heater gas and fugitive emissions. The catalysts used in catalytic reforming processes are usually very expensive and extra precautions are taken to ensure that catalyst is not lost. When the catalyst has lost its activity and can no longer be regenerated, the catalyst is usually sent off-site for recovery of the metals.⁵² Subsequent air emissions from catalyst regeneration is, therefore, relatively low. Relatively small volumes of wastewater containing sulfides, ammonia, and mercaptans may be generated from the stripping tower used to remove light ends from the reactor effluent.⁵³

Solvent Extraction

Solvent extraction uses solvents to dissolve and remove aromatics from lube oil feed stocks, improving viscosity, oxidation resistance, color and gum formation. A number of different solvents are used with the two most common being furfural and phenol. Typically, feed lube stocks are contacted with the solvent in a packed tower or rotating disc contactor. Each solvent has a different solvent-to-oil ratio and recycle ratio within the tower. Solvents are recovered from the oil stream through distillation and steam stripping in a fractionator. The stream extracted from the solvent will likely contain high concentrations of hydrogen sulfide, aromatics, naphthenes and other hydrocarbons, and is often fed to the hydrocracking unit. The water stream leaving the fractionator will likely contain some oil and solvents.⁵⁴

Chemical Treating

In petroleum refining, chemical treating is used to remove or change the undesirable properties associated with sulfur, nitrogen, or oxygen compound contaminants in petroleum products. Chemical treating is accomplished by either extraction or oxidation (also known as sweetening), depending upon the product. Extraction is used to remove sulfur from the very light petroleum fractions, such as propane/propylene (PP) and butane/butylene (BB). Sweetening, though, is more effective on gasoline and middle distillate products.

A typical extraction process is "Merox" extraction. Merox extraction is used to remove mercaptans (organic sulfur compounds) from PP and BB streams. PP streams may undergo amine treating before the Merox

extraction to remove excess H_2S which tends to fractionate with PP and interferes with the Merox process. A caustic prewash of the PP and BB removes any remaining trace H_2S prior to Merox extraction.

The PP and BB streams are passed up through the trays of an extraction tower. Caustic solution flowing down the extraction tower absorbs mercaptan from the PP and BB streams. The rich caustic is then regenerated by oxidizing the mercaptans to disulfide in the presence of aqueous Merox catalyst and the lean caustic recirculated to the extraction tower. The disulfide is insoluble in the caustic and can be separated.

Oxidation or "sweetening" is used on gasoline and distillate fractions. A common oxidation process is also a Merox process that uses a solid catalyst bed. Air and a minimum amount of alkaline caustic ("mini-alky" operation) is injected into the hydrocarbon stream. As the hydrocarbon passes through the Merox catalyst bed, sulfur mercaptans are oxidized to disulfide. In the sweetening Merox process, the caustic is not regenerated. The disulfide can remain with the gasoline product, since it does not possess the objectionable odor properties of mercaptans; hence, the product has been "sweetened."⁵⁵

In the extraction process, a waste oily disulfide stream leaves the separator. Air emissions arise from fugitive hydrocarbons and the process vents on the separator which may contain disulfides.⁵⁶

Dewaxing

Dewaxing of lubricating oil base stocks is necessary to ensure that the oil will have the proper viscosity at lower ambient temperatures. Two types of dewaxing processes are used: selective hydrocracking and solvent dewaxing. In selective hydrocracking, one or two zeolite catalysts are used to selectively crack the wax paraffins. Solvent dewaxing is more prevalent. In solvent dewaxing, the oil feed is diluted with solvent to lower the viscosity, chilled until the wax is crystallized, and then filtered to remove the wax. Solvents used for the process include propane and mixtures of methyl ethyl ketone (MEK) with methyl isobutyl ketone (MIBK) or MEK with toluene. Solvent is recovered from the oil and wax through heating, two-stage flashing, followed by steam stripping. The solvent recovery stage results in solvent contaminated water which typically is sent to the wastewater treatment plant. The wax is either used as feed to the catalytic cracker or is deoiled and sold as industrial wax. Air emissions may arise from fugitive emissions of the solvents.⁵⁷

Propane Deasphalting

Propane deasphalting produces lubricating oil base stocks by extracting asphaltenes and resins from the residuals of the vacuum distillation unit. Propane is usually used to remove asphaltenes due to its unique solvent properties. At lower temperatures (100 to 140 degrees F), paraffins are very soluble in propane and at higher temperatures (about 200 degrees F) all hydrocarbons are almost insoluble in propane. The propane deasphalting process is similar to solvent extraction in that a packed or baffled extraction tower or rotating disc contactor is used to mix the oil feed stocks with the solvent. In the tower method, four to eight volumes of propane are fed to the bottom of the tower for every volume of feed flowing down from the top of the tower. The oil, which is more soluble in the propane dissolves and flows to the top. The asphaltene and resins flow to the bottom of the tower where they are removed in a propane mix. Propane is recovered from the two streams through two-stage flash systems followed by steam stripping in which propane is condensed and removed by cooling at high pressure in the first stage and at low pressure in the second stage. The asphalt recovered can be blended with other asphalts or heavy fuels, or can be used as feed to the coker. The propane recovery stage results in propane contaminated water which typically is sent to the wastewater treatment plant. Air emissions may arise from fugitive propane emissions and process vents.⁵⁸

III.A.3. Supporting Operations

Many important refinery operations are not directly involved in the production of hydrocarbon fuels but serve in a supporting role. Some of the major supporting processes are discussed below.

Wastewater Treatment

Relatively large volumes of water are used by the petroleum refining industry. Four types of wastewater are produced: surface water runoff, cooling water, process water, and sanitary wastewater. Surface water runoff is intermittent and will contain constituents from spills to the surface, leaks in equipment and any materials that may have collected in drains. Runoff surface water also includes water coming from crude and product storage tank roof drains.

A large portion of water used in petroleum refining is used for cooling. Cooling water typically does not come into direct contact with process oil

streams and therefore contains less contaminants than process wastewater. Most cooling water is recycled over and over with a bleed or blowdown stream to the wastewater treatment unit to control the concentration of contaminants and the solids content in the water. Cooling towers within the recycle loop cool the water using ambient air. (See *Storage Tanks and Cooling Towers*) Some cooling water, termed “once through,” is passed through a process unit once and is then discharged directly without treatment in the wastewater treatment plant. The water used for cooling often contains chemical additives such as chromates, phosphates, and antifouling biocides to prevent scaling of pipes and biological growth. (It should be noted, however, that many refineries no longer use chromates in cooling water as anti-fouling agents.) Although cooling water usually does not come into direct contact with oil process streams, it also may contain some oil contamination due to leaks in the process equipment.⁵⁹

Water used in processing operations also accounts for a significant portion of the total wastewater. Process wastewater arises from desalting crude oil, steam stripping operations, pump gland cooling, product fractionator reflux drum drains and boiler blowdown. Because process water often comes into direct contact with oil, it is usually highly contaminated.⁶⁰

Petroleum refineries typically utilize primary and secondary wastewater treatment. Primary wastewater treatment consists of the separation of oil, water and solids in two stages. During the first stage, an API separator, a corrugated plate interceptor, or other separator design is used. Wastewater moves very slowly through the separator allowing free oil to float to the surface and be skimmed off, and solids to settle to the bottom and be scraped off to a sludge collecting hopper. The second stage utilizes physical or chemical methods to separate emulsified oils from the wastewater. Physical methods may include the use of a series of settling ponds with a long retention time, or the use of dissolved air flotation (DAF). In DAF, air is bubbled through the wastewater, and both oil and suspended solids are skimmed off the top. Chemicals, such as ferric hydroxide or aluminum hydroxide, can be used to coagulate impurities into a froth or sludge which can be more easily skimmed off the top. Some wastes associated with the primary treatment of wastewater at petroleum refineries may be considered hazardous and include: API separator sludge, primary treatment sludge, sludges from other gravitational separation techniques, float from DAF units, and wastes from settling ponds (Exhibit 13).⁶¹

After primary treatment, the wastewater can be discharged to a publicly owned treatment works or undergo secondary treatment before being discharged directly to surface waters under a National Pollution Discharge

Elimination System (NPDES) permit. In secondary treatment, dissolved oil and other organic pollutants may be consumed biologically by microorganisms. Biological treatment may require the addition of oxygen through a number of different techniques, including activated sludge units, trickling filters, and rotating biological contactors. Secondary treatment generates bio-mass waste which is typically treated anaerobically, and then dewatered.⁶²

Some refineries employ an additional stage of wastewater treatment called polishing to meet discharge limits. The polishing step can involve the use of activated carbon, anthracite coal, or sand to filter out any remaining impurities, such as biomass, silt, trace metals and other inorganic chemicals, as well as any remaining organic chemicals.^{63,64}

Certain refinery wastewater streams are treated separately, prior to the wastewater treatment plant, to remove contaminants that would not easily be treated after mixing with other wastewater. One such waste stream is the sour water drained from distillation reflux drums. Sour water contains dissolved hydrogen sulfide and other organic sulfur compounds and ammonia which are stripped in a tower with gas or steam before being discharged to the wastewater treatment plant.⁶⁵

Wastewater treatment plants are a significant source of refinery air emissions and solid wastes. Air releases arise from fugitive emissions from the numerous tanks, ponds and sewer system drains. Solid wastes are generated in the form of sludges from a number of the treatment units.

Gas Treatment and Sulfur Recovery

Sulfur is removed from a number of refinery process off-gas streams (sour gas) in order to meet the SO_x emissions limits of the CAA and to recover saleable elemental sulfur. Process off-gas streams, or sour gas, from the coker, catalytic cracking unit, hydrotreating units and hydroprocessing units can contain high concentrations of hydrogen sulfide mixed with light refinery fuel gases. Before elemental sulfur can be recovered, the fuel gases (primarily methane and ethane) need to be separated from the hydrogen sulfide. This is typically accomplished by dissolving the hydrogen sulfide in a chemical solvent. Solvents most commonly used are amines, such as diethanolamine (DEA). Dry adsorbents such as molecular sieves, activated carbon, iron sponge and zinc oxide are also used. In the amine solvent processes, DEA solution or another amine solvent is pumped to an absorption tower where the gases are contacted and hydrogen sulfide is dissolved in the solution. The fuel gases are removed for use as fuel in process furnaces in other refinery operations. The amine-hydrogen sulfide solution is then heated and steam stripped to remove the hydrogen sulfide gas.⁶⁶

Current methods for removing sulfur from the hydrogen sulfide gas streams are typically a combination of two processes: the Claus Process followed by the Beaven Process, Scot Process, or the Wellman-Land Process. The Claus process consists of partial combustion of the hydrogen sulfide-rich gas stream (with one-third the stoichiometric quantity of air) and then reacting the resulting sulfur dioxide and unburned hydrogen sulfide in the presence of a bauxite catalyst to produce elemental sulfur (Exhibit 14).

Since the Claus process by itself removes only about 90 percent of the hydrogen sulfide in the gas stream, the Beaven, SCOT, or Wellman-Lord processes are often used to further recover sulfur. In the Beaven process, the hydrogen sulfide in the relatively low concentration gas stream from the Claus process can be almost completely removed by absorption in a quinone solution. The dissolved hydrogen sulfide is oxidized to form a mixture of elemental sulfur and hydro-quinone. The solution is injected with air or oxygen to oxidize the hydro-quinone back to quinone. The solution is then filtered or centrifuged to remove the sulfur and the quinone is then reused. The Beaven process is also effective in removing small amounts of sulfur dioxide, carbonyl sulfide, and carbon disulfide that are not affected by the Claus process. These compounds are first converted to hydrogen sulfide at elevated temperatures in a cobalt molybdate catalyst prior to being fed to the Beaven unit.^{67,68} Air emissions from sulfur

recovery units will consist of hydrogen sulfide, SO_x and NO_x in the process tail gas as well as fugitive emissions and releases from vents.

The SCOT process is also widely used for removing sulfur from the Claus tail gas. The sulphur compounds in the Claus tail gas are converted to hydrogen sulfide by heating and passing it through a cobalt-molybdenum catalyst with the addition of a reducing gas. The gas is then cooled and contacted with a solution of di-isopropanolamine (DIPA) which removes all but trace amounts of hydrogen sulfide. The sulfide-rich DIPA is sent to a stripper where hydrogen sulfide gas is removed and sent to the Claus plant. The DIPA is returned to the absorption column.

Additive Production

A number of chemicals (mostly alcohols and ethers) are added to motor fuels to either improve performance or meet federal and state environmental requirements. Since the 1970s, alcohols (methanol and ethanol) and ethers have been added to gasoline to increase octane levels and reduce carbon monoxide generation in place of the lead additives which were being phased out as required by the 1970 Clean Air Act. In 1990, the more stringent Clean Air Act Amendments (see Section V.B) established minimum and maximum amounts of chemically combined oxygen in motor fuels as well as an upper limit on vapor pressure. As a result, alcohol additives have been increasingly supplemented or replaced with a number of different ethers which are better able to meet both the new oxygen requirements and the vapor pressure limits.

The most common ethers being used as additives are methyl tertiary butyl ether (MTBE), and tertiary amyl methyl ether (TAME). Many of the larger refineries manufacture their own supplies of MTBE and TAME by reacting isobutylene and/or isoamylene with methanol. Smaller refineries usually buy their supplies from chemical manufacturers or the larger refineries. Isobutylene is obtained from a number of refinery sources including: the light naphtha from the FCCU and coking units, the by-product from steam cracking of naphtha or light hydrocarbons during the production of ethylene and propylene, catalytic dehydrogenation of isobutane, and conversion of tertiary butyl alcohol recovered as a by-product in the manufacture of propylene oxides. Several different processes are currently in use to produce MTBE and TAME from isobutylene and methanol. Most processes use a two-stage acidic ion exchange resin catalyst. The reaction is exothermic and cooling to the proper reaction temperature is critical in obtaining the optimal conversion efficiency. The process usually produces an MTBE or TAME stream and a relatively small stream of unreacted hydrocarbons and methanol. The

methanol is extracted in a water wash and the resulting methanol-water mixture is distilled to recover the methanol for recycling.

Heat Exchanger Cleaning

Heat exchangers are used throughout petroleum refineries to heat or cool petroleum process streams. The heat exchangers consist of bundles of pipes, tubes, plate coils, or steam coils enclosing heating or cooling water, steam, or oil to transfer heat indirectly to or from the oil process stream. The bundles are cleaned periodically to remove accumulations of scales, sludge and any oily residues. Because chromium has almost been eliminated as a cooling water additive, wastes generated from the cleaning of heat exchanger bundles no longer account for a significant portion of the hazardous wastes generated at refining facilities. The sludge generated may contain lead or chromium, although some refineries which do not produce leaded gasoline and which use non-chrome corrosion inhibitors typically do not generate sludge that contains these constituents. Oily wastewater is also generated during heat exchanger cleaning.⁶⁹

Blowdown System

Most refinery process units and equipment are manifolded into a collection unit, called the blowdown system. Blowdown systems provide for the safe handling and disposal of liquid and gases that are either automatically vented from the process units through pressure relief valves, or that are manually drawn from units. Recirculated process streams and cooling water streams are often manually purged to prevent the continued build up of contaminants in the stream. Part or all of the contents of equipment can also be purged to the blowdown system prior to shutdown before normal or emergency shutdowns. Blowdown systems utilize a series of flash drums and condensers to separate the blowdown into its vapor and liquid components. The liquid is typically composed of mixtures of water and hydrocarbons containing sulfides, ammonia, and other contaminants, which are sent to the wastewater treatment plant. The gaseous component typically contains hydrocarbons, hydrogen sulfide, ammonia, mercaptans, solvents, and other constituents, and is either discharged directly to the atmosphere or is combusted in a flare. The major air emissions from blowdown systems are hydrocarbons in the case of direct discharge to the atmosphere and sulfur oxides when flared.

Blending

Blending is the final operation in petroleum refining. It consists of mixing the products in various proportions to meet specifications such as vapor

pressure, specific gravity, sulfur content, viscosity, octane number, cetane index, initial boiling point, and pour point. Blending can be carried out in-line or in batch blending tanks. Air emissions from blending are fugitive VOCs from blending tanks, valves, pumps and mixing operations.⁷⁰

Storage Tanks

Storage tanks are used throughout the refining process to store crude oil and intermediate process feeds for cooling and further processing. Finished petroleum products are also kept in storage tanks before transport off site. Storage tank bottoms are mixtures of iron rust from corrosion, sand, water, and emulsified oil and wax, which accumulate at the bottom of tanks. Liquid tank bottoms (primarily water and oil emulsions) are periodically drawn off to prevent their continued build up. Tank bottom liquids and sludge are also removed during periodic cleaning of tanks for inspection. Tank bottoms may contain amounts of tetraethyl or tetramethyl lead (although this is increasingly rare due to the phaseout of leaded products), other metals, and phenols. Solids generated from leaded gasoline storage tank bottoms are listed as a RCRA hazardous waste.^{71,72}

Even if equipped with floating tops, storage tanks account for considerable VOC emissions at petroleum refineries. A study of petroleum refinery emissions found that the majority of tank losses occurred through tank seals on gasoline storage tanks.⁷³

Cooling Towers

Cooling towers cool heated water by circulating the water through a tower with a predetermined flow of ambient air pushed with large fans. A certain amount of water exits the system through evaporation, mist droplets and as bleed or blowdown to the wastewater treatment system. Therefore, make-up water in the range of about five percent of the circulation rate is required.⁷⁴

III.B. Raw Material Inputs and Pollution Outputs in the Production Line

Raw material input to petroleum refineries is primarily crude oil; however, petroleum refineries use and generate an enormous number of chemicals, many of which leave the facilities as discharges of air emissions, wastewater, or solid waste. Pollutants generated typically include VOCs, carbon monoxide (CO), sulfur oxides (SO_x), nitrogen oxides (NO_x), particulates, ammonia (NH₃), hydrogen sulfide (H₂S), metals, spent acids,

and numerous toxic organic compounds. Exhibit 15 summarizes the main pollutant outputs for each major refinery process.

When discussing material outputs of the petroleum refining industry, it is important to note the relationship between the outputs of the industry itself and the outputs resulting from the use of refinery products. Petroleum refineries play an important role in the U.S. economy, supplying approximately 40 percent of the total energy used in the U.S. and virtually all of the energy consumed in the transportation sector. The pollutant outputs from the refining facilities, however, are modest in comparison to the pollutant outputs realized from the consumption of petroleum products by the transportation sector, electric utilities, chemical manufacturers and other industrial and commercial users.

Air Emissions

Air emissions from refineries include fugitive emissions of the volatile constituents in crude oil and its fractions, emissions from the burning of fuels in process heaters, and emissions from the various refinery processes themselves. Fugitive emissions occur throughout refineries and arise from the thousands of potential fugitive emission sources such as valves, pumps, tanks, pressure relief valves, flanges, etc. While individual leaks are typically small, the sum of all fugitive leaks at a refinery can be one of its largest emission sources. Fugitive emissions can be reduced through a number of techniques, including improved leak resistant equipment, reducing the number of tanks and other potential sources and, perhaps the most effective method, an ongoing Leak Detection and Repair (LDAR) program.

The numerous process heaters used in refineries to heat process streams or to generate steam (boilers) for heating or steam stripping, can be potential sources of SO_x, NO_x, CO, particulates and hydrocarbons emissions. When operating properly and when burning cleaner fuels such as refinery fuel gas, fuel oil or natural gas, these emissions are relatively low. If, however, combustion is not complete, or heaters are fired with refinery fuel pitch or residuals, emissions can be significant.⁷⁵

The majority of gas streams exiting each refinery process contain varying amounts of refinery fuel gas, hydrogen sulfide and ammonia. These streams are collected and sent to the gas treatment and sulfur recovery units to recover the refinery fuel gas and sulfur. Emissions from the sulfur recovery unit typically contains some H₂S, SO_x and NO_x. Other emissions sources from refinery processes arise from periodic regeneration of catalysts. These processes generate streams that may contain relatively

high levels of carbon monoxide, particulates and VOCs. Before being discharged to the atmosphere, such off-gas streams may be treated first through a carbon monoxide boiler to burn carbon monoxide and any VOCs, and then through an electrostatic precipitator or cyclone separator to remove particulates.⁷⁶

Wastewater

Wastewaters consist of cooling water, process water, sanitary sewage water, and storm water. Wastewaters are treated in onsite wastewater treatment facilities and then discharged to POTWs or discharged to surface waters under NPDES permits. In addition, some facilities use underground injection of some wastewater streams. (See Wastewater Treatment in Section III.A.)

Many refineries unintentionally release, or have unintentionally released in the past, liquid hydrocarbons to ground water and surface waters. At some refineries contaminated ground water has migrate off-site and resulted in continuous “seeps” to surface waters. While the actual volume of hydrocarbons released in such a manner are relatively small, there is the potential to contaminate large volumes of ground water and surface water possibly posing a substantial risk to human health and the environment.

Other Wastes

Other wastes are generated from many of the refining processes, petroleum handling operations, as well as wastewater treatment. Both hazardous and non-hazardous wastes are generated, treated and disposed. Residual refinery wastes are typically in the form of sludges, spent process catalysts, filter clay, and incinerator ash. Treatment of these wastes includes incineration, land treating off-site, land filling onsite, land filling off-site, chemical fixation, neutralization, and other treatment methods.

A significant portion of the non-petroleum product outputs of refineries is transported off-site and sold as byproducts. These outputs include sulfur, acetic acid, phosphoric acid, and recovered metals. Metals from catalysts and from the crude oil that have deposited on the catalyst during the production often are recovered by third party recovery facilities.

Exhibit 15: Typical Material Outputs from Selected Petroleum Refining Processes			
Process	Air Emissions	Process Waste Water	Residual Wastes Generated
Crude oil desalting	Heater stack gas (CO, SO _x , NO _x , hydrocarbons and particulates), fugitive emissions (hydrocarbons)	Flow=2.1 Gal/Bbl Oil, H ₂ S, NH ₃ , phenol, high levels of suspended solids, dissolved solids, high BOD, high temperature.	Crude oil/desalter sludge (iron rust, clay, sand, water, emulsified oil and wax, metals)
Atmospheric distillation	Heater stack gas (CO, SO _x , NO _x , hydrocarbons and particulates), vents and fugitive emissions (hydrocarbons)	Flow=26.0 Gal/Bbl Oil, H ₂ S, NH ₃ , suspended solids, chlorides, mercaptans, phenol, elevated pH.	Typically, little or no residual waste generated.
Vacuum Distillation	Steam ejector emissions (hydrocarbons), heater stack gas (CO, SO _x , NO _x , hydrocarbons and particulates), vents and fugitive emissions (hydrocarbons)		
Thermal Cracking/ Visbreaking	Heater stack gas (CO, SO _x , NO _x , hydrocarbons and particulates), vents and fugitive emissions (hydrocarbons).	Flow=2.0 Gal/Bbl Oil, H ₂ S, NH ₃ , phenol, suspended solids, high pH, BOD ₅ , COD.	Typically, little or no residual waste generated.
Coking	Heater stack gas (CO, SO _x , NO _x , hydrocarbons and particulates), vents and fugitive emissions (hydrocarbons) and decoking emissions (hydrocarbons and particulates).	Flow=1.0 Gal/Bbl High pH, H ₂ S, NH ₃ , suspended solids, COD.	Coke dust (carbon particles and hydrocarbons)
Catalytic Cracking	Heater stack gas (CO, SO _x , NO _x , hydrocarbons and particulates), fugitive emissions (hydrocarbons) and catalyst regeneration (CO, NO _x , SO _x , and particulates)	Flow=15.0 Gal/Bbl High levels of oil, suspended solids, phenols, cyanides, H ₂ S, NH ₃ , high pH, BOD, COD.	Spent catalysts (metals from crude oil and hydrocarbons), spent catalyst fines from electrostatic precipitators (aluminum silicate and metals)

Exhibit 15: Typical Material Outputs from Selected Petroleum Refining Processes			
Catalytic Hydro-cracking	Heater stack gas (CO, SO _x , NO _x , hydrocarbons and particulates), fugitive emissions (hydrocarbons) and catalyst regeneration (CO, NO _x , SO _x and catalyst dust).	Flow=2.0 Gal/Bbl High COD, suspended solids, H ₂ S, relatively low levels of BOD.	Spent catalysts fines (metals from crude oil, and hydrocarbons)
Hydrotreating/ Hydroprocessing	Heater stack gas (CO, SO _x , NO _x , hydrocarbons and particulates), vents and fugitive emissions (hydrocarbons) and catalyst regeneration (CO, NO _x , SO _x)	Flow=1.0 Gal/Bbl H ₂ S, NH ₃ , High pH, phenols suspended solids, BOD, COD.	Spent catalyst fines (aluminum silicate and metals).
Alkylation	Heater stack gas (CO, SO _x , NO _x , hydrocarbons and particulates), vents and fugitive emissions (hydrocarbons)	Low pH, suspended solids, dissolved solids, COD, H ₂ S, spent sulfuric acid.	Neutralized alkylation sludge (sulfuric acid or calcium fluoride, hydrocarbons).
Isomerization	Heater stack gas (CO, SO _x , NO _x , hydrocarbons and particulates), HCl (potentially in light ends), vents and fugitive emissions (hydrocarbons)	Low pH, chloride salts, caustic wash, relatively low H ₂ S and NH ₃ .	Calcium chloride sludge from neutralized HCl gas.
Polymerization	H ₂ S from caustic washing	H ₂ S, NH ₃ , caustic wash, mercaptans and ammonia, high pH.	Spent catalyst containing phosphoric acid.
Catalytic Reforming	Heater stack gas (CO, SO _x , NO _x , hydrocarbons and particulates), fugitive emissions (hydrocarbons) and catalyst regeneration (CO, NO _x , SO _x)	Flow=6.0 Gal/Bbl High levels oil, suspended solids, COD. Relatively low H ₂ S.	Spent catalyst fines from electrostatic precipitators (alumina silicate and metals).
Solvent Extraction	Fugitive solvents	Oil and solvents	Little or no residual wastes generated.
Dewaxing	Fugitive solvents, heaters	Oil and solvents	Little or no residual wastes generated.
Propane Deasphalting	Heater stack gas (CO, SO _x , NO _x , hydrocarbons and particulates), fugitive propane	Oil and propane	Little or no residual wastes generated.
Mercox treating	Vents and fugitive emissions (hydrocarbons and disulfides).	Little or no wastewater generated.	Spent Mercox caustic solution, waste oil-disulfide mixture.

Exhibit 15: Typical Material Outputs from Selected Petroleum Refining Processes			
Wastewater treatment	Fugitive emissions (H ₂ S, NH ₃ , and hydrocarbons)	Not Applicable	API separator sludge (phenols, metals and oil), chemical precipitation sludge (chemical coagulants, oil), DAF floats, biological sludges (metals, oil, suspended solids), spent lime.
Gas Treatment and Sulfur Recovery	SO _x , NO _x , and H ₂ S from vent and tail gas emissions.	H ₂ S, NH ₃ , amines, Stretford solution.	Spent catalyst.
Blending	Fugitive emissions (hydrocarbons)	Little or no wastewater generated	Little or no residual waste generated.
Heat exchanger cleaning	Periodic fugitive emissions (hydrocarbons)	Oily wastewater generated	Heat exchanger sludge (oil, metals, and suspended solids)
Storage Tanks	Fugitive emissions (hydrocarbons)	Water drained from tanks contaminated with tank product	Tank bottom sludge (iron rust, clay, sand, water, emulsified oil and wax, metals)
Blowdown and flare	Combustion products (CO, SO _x , NO _x and hydrocarbons) from flares, fugitive emissions	Little or no wastewater generated	Little or no residual waste generated.
Sources: <i>Assessment of Atmospheric Emissions from Petroleum Refining</i> , Radian Corp., 1980; <i>Petroleum Refining Hazardous Waste Generation</i> , U.S. EPA, Office of Solid Waste, 1994.			

III.C. Management of Chemicals in Wastestream

The Pollution Prevention Act of 1990 (PPA) requires facilities to report information about the management of TRI chemicals in waste and efforts made to eliminate or reduce those quantities. These data have been collected annually in Section 8 of the TRI reporting Form R beginning with the 1991 reporting year. The data summarized below cover the years 1992-1995 and is meant to provide a basic understanding of the quantities of waste handled by the industry, the methods typically used to manage this waste, and recent trends in these methods. TRI waste management data can be used to assess trends in source reduction within individual industries and facilities, and for specific TRI chemicals. This information could then be used as a tool in identifying opportunities for pollution prevention compliance assistance activities.

From the yearly data presented below it is apparent that the portion of TRI wastes reported as recycled on-site has increased and the portions treated or managed through energy recovery on-site have decreased between 1992 and 1995 (projected). While the quantities reported for 1992 and 1993 are estimates of quantities already managed, the quantities reported for 1994 and 1995 are projections only. The PPA requires these projections to encourage facilities to consider future waste generation and source reduction of those quantities as well as movement up the waste management hierarchy. Future-year estimates are not commitments that facilities reporting under TRI are required to meet.

Exhibit 16 shows that the petroleum refining industry managed about 1.6 billion pounds of production-related waste (total quantity of TRI chemicals in the waste from routine production operations) in 1993 (column B). Column C reveals that of this production-related waste, 30 percent was either transferred off-site or released to the environment. Column C is calculated by dividing the total TRI transfers and releases by the total quantity of production-related waste. In other words, about 70 percent of the industry's TRI wastes were managed on-site through recycling, energy recovery, or treatment as shown in columns E, F and G, respectively. The majority of waste that is released or transferred off-site can be divided into portions that are recycled off-site, recovered for energy off-site, or treated off-site as shown in columns H, I and J, respectively. The remaining portion of the production related wastes (4 percent), shown in column D, is either released to the environment through direct discharges to air, land, water, and underground injection, or it is disposed of off-site.

Exhibit 16: Source Reduction and Recycling Activity for Petroleum Industry (SIC 2911) as Reported within TRI									
A	B	C	D	On-Site			Off-Site		
Year	Quantity of Production-Related Waste (10 ⁶ lbs.) ^a	% Released and Transferred ^b	% Released and Disposed ^c Off-site	E	F	G	H	I	J
				% Recycled	% Energy Recovery	% Treated	% Recycled	% Energy Recovery	% Treated
1992	1,476	24%	3%	10%	37%	22%	27%	<1%	<1%
1993	1,600	30%	4%	14%	36%	20%	26%	<1%	<1%
1994	1,867	---	4%	19%	37%	15%	25%	<1%	<1%
1995	1,717	---	4%	21%	32%	17%	27%	<1%	<1%

- ^a Within this industry sector, non-production related waste < 1 percent of production related wastes for 1993.
- ^b Total TRI transfers and releases as reported in Sections 5 and 6 of Form R as a percentage of production related wastes.
- ^c Percentage of production related waste released to the environment and transferred off-site for disposal.